New Developments On Laser Heated Diamond Anvil Cell

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New developments on laser heated diamond anvil cell are reported by introducing a system installed at the Advanced Photon Source (APS). With the system, a laser heating spot of 20 - 40 µm in diameter can be generated to temperatures over 3000 K for samples in diamond anvil cell; and the temperature gradients in the laser heated volume are less than 100 K. The system is based on the double sided laser heating technique, including (a) a heating laser system consisting of two Nd:YLF lasers with one operating in TEM_{00} and the other in TEM_{01}*, (b) Kaiser holographic spectrometers together with the charge coupled device (CCD) for temperature measurement, and (c) optics that allows to combine various x-ray measurements. The system has been used to obtain *in situ* high P-T x-ray diffraction on metals, oxides, and silicates to temperatures over 3000 K and to pressures of 160 GPa.
[diamond anvil cell, laser heating, x-ray diffraction, synchrotron, spectral radiometry]

1. Introduction

Because of the transparency of the diamond window, laser heating technique has been widely used for generating ultra high temperatures in diamond anvil cell (DAC). Since the pioneering work of Ming and Bassett [1], this technique has been applied in synthesis of high P-T phases [2, 3], phase transition studies [4, 5], high pressure melting [4, 6, 7] and in situ x-ray diffraction at high P-T [8, 9]. The development of the laser heating technique is mainly reflected by the precision and accuracy of temperature measurements, the temperature stability, and the temperature gradients in both the radial and axial directions. The spectral radiometry technique [10, 11] significantly increased the precision and accuracy of temperature measurement. The use of stable CW lasers and the introduction of feedback systems [12, 13] improved the temperature stability. The double sided laser heating technique using powerful multimode lasers largely reduced the temperature gradients both radially and axially [14, 15]. In this paper, we will discuss on each development and describe our efforts on further improvement. The developed system has been installed at the GeoSoilEnviroCARS sector at the APS, where the laser heated DAC has been combined to the synchrotron x-ray beam for a variety of *in situ* high P-T x-ray measurements.

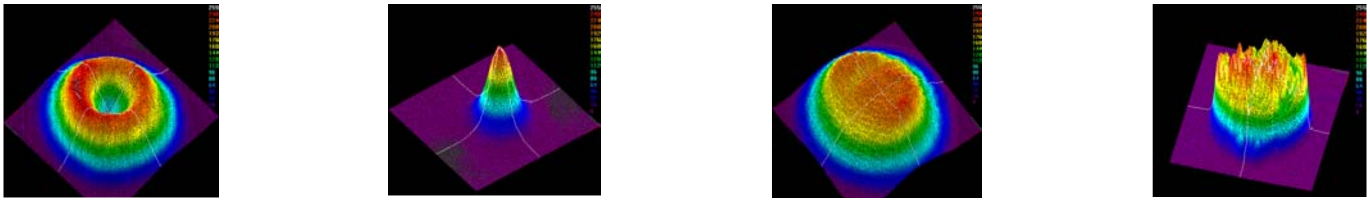
2. Description of the Laser Heating System

Heating Lasers

Diamond is of the highest thermal conductivity among known materials. To heat samples at high pressure between two diamond anvils, lasers should have sufficiently high power and low divergence to be able to focus down to a desired size and to have enough photon density. Fundamental mode (TEM_{00}) laser is therefore often used for laser heated DAC because it provides a laser beam with high collimation and stability. The drawback of using TEM_{00} mode laser is the temperature gradient of a heated spot resulting from the Gaussian intensity distribution. Multimode lasers [14] can provide over 100 W beam with a relatively flat top in intensity profile, allowing to generate a large heating spot with little temperature gradient. Compared to the single mode lasers, multimode lasers have a relative large beam divergence and power instability. Furthermore, multimode laser is normally not polarized, which lead to difficulties in building fast response feed back system. We have developed a laser system consisting of two Nd:YLF lasers with one operating in TEM_{01}* mode (donut mode) and the other in TEM_{00} mode. Some specifications of these two lasers are listed in Table 1. The combined beam of the two Nd:YLF lasers gives a total power of 105 W, comparable to that of multimode lasers and more than 3 times larger than that of generally used TEM_{00} YAG (or YLF) lasers. As shown in Table 1, the YLF lasers provide high brightness beams as reflected by small beam diameter, low divergence, and high power. The power stability and, especially, the pointing stability are far superior to those of YAG lasers, a crucial factor to have a heating spot at steady temperature and at constant position. Very importantly, the two-laser system allows us to *construct* a desired beam profile of heating laser and, as a result, a laser heating spot with minimum radial temperature gradients in the central heating area (~20 µm in diameter). Figure 1 shows the intensity profiles measured from these two lasers. By adjusting mixture power ratios of two lasers, for example, a flat top within 5% in power intensity can be reached (Figure 1c). Figure 1d shows the intensity profile with the multimode output for comparison. It is clear that the constructed beam (TEM_{00} + TEM_{01}*) is much smoother than the multimode laser beam.

Table 1. Performance of two Nd:YLF lasers

Laser mode	TEM_{00}	TEM_{01}*
Output Power	50 W	65 W
Power instability	<1% p-p	<1% p-p
Beam pointing instability	x: <30 µrad y: <30 µrad	x: <30 µrad y: <30 µrad
Wavelength	1053 nm	1053 nm
Divergence	1.5 mrad	1.8 mrad
Beam diameter	1 mm	1.2 mm
Roundness	>0.95	>0.95



TEM_{01}* Donut Mode **(a)** **TEM_{00} Gaussian Mode** **(b)** **TEM_{01}* + TEM_{00}** **(c)** **Multimode** **(d)**

Figure 1. Beam intensity profiles in three dimension of Nd:YLF lasers measured by a laser beam analyzer.

Optics Setup

The guiding optics includes power regulators, combining optics, laser power detector, beam splitter, and focusing. A schematic diagram of the optical system is shown in Figure 2. The two laser beams with different polarization allow combining two beams into one by a cube beamsplitter (bs2). The combined beam is then split into two by a non-polarized cube beamsplitter (bs3) and guided to the sample from both ends of the DAC. A beryllium mirror (M5) coated with silver is employed between the objective lens and sample position. This mirror functions to guide laser beam, and receive sample image and thermal radiation signals, while allowing the x-rays to pass through. With the proper coaxial setup between the dichroic mirror (M3) and the sample position, adjusting the beryllium mirror will not affect the internal alignment between the laser heating spot and the image used for temperature measurement. Thus the beryllium mirror allows adjusting the sample to the x-ray position where the heating laser beam will be applied and the temperature measured.

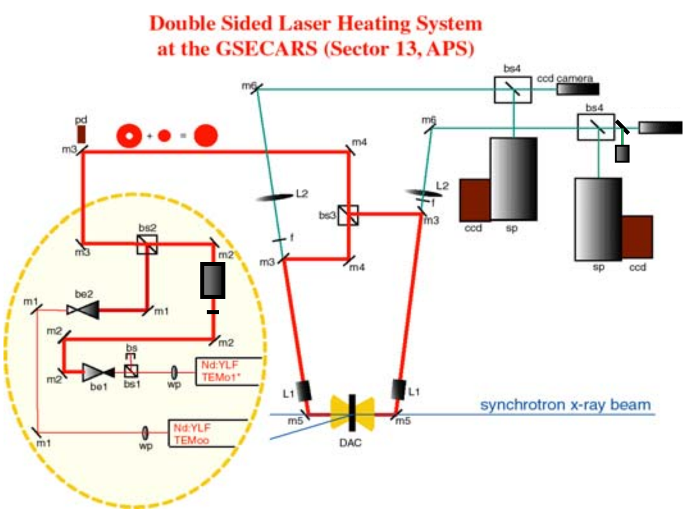


Figure 2. Schematics of the double sided laser heating system

The sample image is collected by an apochromat (L1) and focused with an achromatic lens (L2, f=1000 mm). L1 and L2 provide a magnification of about 17x. A 50/50 beamsplitter (bs4) is used, with one transmitted branch for viewing by a CCD camera and the other reflected branch for spectroscopic measurement (sp). Use of reflected branch avoids introducing chromatic aberration. The spectroradiometric system consists of a thermodynamically cooled CCD detector (Princeton Instruments, TE/CCD-1100PB) and a Kaiser spectrograph (HoloSpec, f/2.2vis). The HFG-750 grating is used, covering the wavelength range of 550-920 nm with central wavelength at 750 nm. When used with an 80 μm entrance slit, the spectrometer gives a wavelength resolution of 1.1 nm. The main advantage of the Kaiser spectrograph is its imaging quality, i.e., the spatial resolution along the direction perpendicular to wavelength dispersion. Because transmission grating is used, Kaiser Holo-spectrograph gives much superior spatial resolution to those with reflected grating. A simple check with a 10 μm thick Au-foil attached to the middle of the entrance slit shows that the image of the edge (FWHM in derivative) is less than 1.5 pixels in the spectrum range of interest from 681 nm to 824 nm. The CCD chip for temperature measurement has 330x1100 pixels, each measuring 27x27 μm across. When another CCD chip with pixel size of 7 μm was used, we got the FWHM of two pixels in the similar spectrum range, indicating that the spatial resolution of the spectrograph is better than the pixel size (27 μm) of the CCD for temperature measurement.

Therefore, the entrance slit of the spectrograph allows a linear image of the sample to be reproduced on the CCD linearly in the direction perpendicular to dispersion. Thus a temperature profile across the heating area can be obtained for each measurement.

3. Discussions

Temperature Measurement

Precision of temperature measurements in laser heated DAC has been much improved with the use of spectral radiometry [10, 11]. In this method, temperatures no longer rely on the absolute emissivity, but are determined by fitting the thermal radiation over certain wavelength range to the Planck radiation function. The system response is calibrated by a tungsten lamp with known radiance.

The accuracy in temperature measurement by spectral radiometry has been validated by many authors [10, 12, 14]. However, these validations are limited to the ambient pressure. Accuracy of temperature measurements at high pressure is still challenging and mainly affected by the wavelength dependence of emissivity and system's chromatic aberration. Some efforts were made to account for the effect of wavelength dependence emissivity by using data at the ambient pressure [7, 10, 13]. Currently, most investigators assume a constant emissivity over the wavelength range being fit to the Planck's radiation function because the emissivity data at high P-T are poorly known. From known emissivity data at 1 atm (e.g., tungsten [16]), the wavelength dependence of emissivity at 2000 K and 3000 K can change the calculated temperature by over 75 K and 200 K, respectively. The lack of wavelength dependence information on emissivity at high P-T limits the accuracy of temperature measurements in the laser heated diamond anvil cell, especially at temperature over 3000 K. Another major source of error in the temperature measurement arises from the temperature gradient in a small hot spot as pointed out by Boehler and Chopelas [17]. If the heating area is uniform, the uncertainty due to the chromatic aberration can be minimized by calibration [14]. High accuracy in temperature measurements critically depends on the uniformity of the heating area. Therefore, our effort on minimizing the temperature gradients in the laser heating spot is not only for establishing a well controlled high T condition in x-ray sampling area, but also for improving the T measurement accuracy.

For laser heated DAC experiments, there is diamond in the optical path. The effect of the diamond window was checked with our system. Radiation from the standard lamp was recorded with and without a diamond anvil. The result indicates that the temperature will be underestimated by 50 - 90 degrees in the temperature range of 2000 - 2700 K if a calibration without a diamond anvil is used in diamond anvil cell experiments. Different diamond anvils (all type-Ia) were tested with thicknesses ranging from 1.6 mm to 2.3 mm. Similar results (within uncertainties <15 K) were obtained. Therefore, for high accuracy, calibration must be done with the specific diamond cell being used in the experiments. In practical applications, however, it seems acceptable to use a calibration with a typical diamond anvil for other DAC experiments.

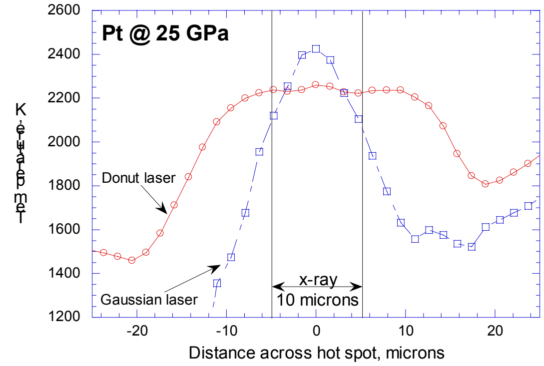


Figure 3. Temperature profiles with TEM_{00} laser and TEM_{01}* laser for platinum at 25 GPa in a DAC. NaCl was used as insulating layers at both sides.

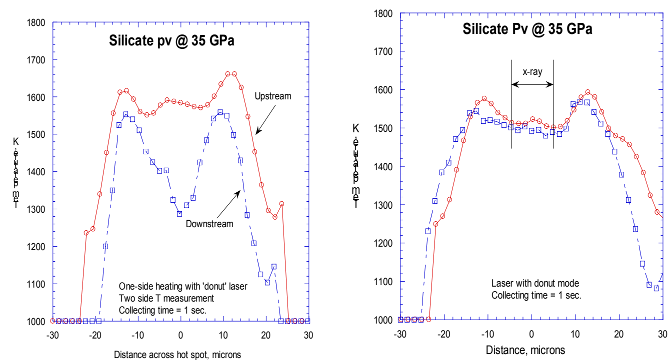


Figure 4. Temperature profiles measured both sides for a silicate perovskite sample at 35 GPa. (a) one sided heating with TEM_{01}* laser; (b) double sided heating with TEM_{01}* laser.

Temperature Gradient

The radial temperature distribution across the heated spot is related to the power distribution of the laser beam, radial heat conduction and the homogeneity of the sample. The radial heat conduction is mainly defined by sample properties. For studying a particular sample, the power distribution of the laser beam is thus a critical factor to ensure an evenly heated area. As shown in Figure 1, our laser system allows us to construct a laser beam with desired power distribution. Use of the TEM_{oo} laser alone resulted in a heating spot with Gaussian temperature profile (Fig. 3). For samples of good heat conductivity (e.g., Pt metal), donut laser often provides a relatively flat-top temperature distribution (Fig. 3). For silicate perovskite, however, a shallow dip can be often seen in temperature profile with the donut laser (Figure 4). In that case, small portion of TEM_{oo} laser can be applied to obtain a more even temperature distribution. Thus, with the two-laser system, the whole system becomes flexible and compatible to different sample conditions. Cautions should be made when applied to samples heated by absorption of the iron content (a few percent) or the mixed absorber (e.g., Pt powder) where diffusion and/or differentiation may occur. The composition inhomogeneity can cause unexpected temperature profiles, a remaining obstacle in having desired radial temperature distribution.

In the loading axis direction, the diamond anvils act as a heat sink and the low temperature boundary. The most severe temperature gradient in the sample exists along the path of the laser beam (axial gradient). The introduction of the double sided laser heating technique [14, 15] took a large step in solving this problem, and this is especially important for in situ x-ray measurement with laser heated DAC. As shown in Fig. 4a, temperatures can differ by a few hundred degrees over a 5 μm thick sample with the single-sided heating method. On the same sample with the double-sided heating technique, the axial gradient is dramatically reduced within experimental uncertainties (Figure 4b).

Stability

Factors affecting temperature stability include the input laser power stability and homogeneity of sample for absorbing to the laser light. For strongly absorbing sample (e.g., Pt foil), the temperature stability is mainly determined by the stability of the input laser power. When a sample is subjected to diffusion or reaction, the temperature is likely to fluctuate even with a perfect stable laser. This instability can be reduced by introducing a feed back system that monitors the thermal radiation from the sample and modulates the laser power accordingly. Standard deviation of 8 K has been reached with a feed back system for laser heated DAC [12].

4. *In Situ* X-Ray Measurements At High P-T

From measured temperature profiles (e.g., Figures 3, 4), the system provides a laser heating spot of 20-30 μm in diameter. At Mbar pressures, the heating area may reduce to 10-20 μm. An x-ray beam of 5 - 10 μm is then required.

Microbeam

X-ray beams of 5-10 μm size can be collimated with a parallel slit system [18]. At GSECARS, the micro-beam is further "cleaned" by another parallel slit system with slightly larger gap (about 5 μm larger). The so-called "clean-up" slits are essential to avoid the beam broadening caused by edge effects from the primary slits. The effectiveness of the clean-up slits has been verified by putting a stainless steel gasket with a hole of 50 μm in diameter on the sample stage. When a 10x10 μm x-ray beam was located at the center of the empty hole without the clean-up slit, gasket diffraction could be clearly detected, whereas the gasket diffraction was eliminated with the clean-up slits in position. The parallel slit system provides a well-collimated x-ray beam, but the total x-ray flux decreases rapidly with decreasing slit size.

For experiments where the high flux density is important, a micro-focusing system consisting of two bent Kirkpatrick-Baez mirrors is used [19]. A 70x70 μm white beam can be easily focused to a 5-10 μm (FWHM) spot with the focusing system. However, the full width at 1% intensity level could be over 30 μm. This "tail" may be cleaned by putting a slit system or pinhole very close to the sample. From Figure 2, because of the laser heating optics, this distance can not be less than 100 mm, resulting in the limitation of beam cleanliness. Depending on specific experiment, our system provides options of slit system for cleanliness or the K-B mirror system for flux.

Alignment

It is clear that proper alignment is crucial for accurate measurements, with all heating, detection, and characterizing systems aligned to the sample position within few microns. For practical applications, we mention two important issues. One is the coaxial arrangement of the laser beam and the thermal radiation path. The other is the optical visibility of the x-ray beam. With coaxial optics, it is possible to adjust sample image using beryllium mirror (M5 in figure 2) without disturbing the internal alignment between the laser beam and the collected thermal radiation. In other words, temperatures are always measured from the heating spot even though the image moves as one adjusts the beryllium mirror. The capability of adjustable image allows us to quickly align the laser heating system to the x-ray position when it becomes optically visible. With the bright APS undulator beam, the luminescence of the sample or pressure medium is often visible through the sensitive CCD camera. For a clear image of the x-ray beam, diamond anvils of low fluorescence are required. The optically visible x-ray image can then be used for alignment to laser heating system.

Applications to Deep Earth Geophysics

A variety of experiments have been performed on deep earth materials, e.g., crystal structures and phase relations of iron up to 160 GPa and 3000 K (Mao et al. in preparation), P-V-T equation of state of $CaSiO_3$ perovskite and $MgSiO_3$ perovskite up to 100 GPa and 2500 K [20], direct density measurement of FeS at Martian's core P-T conditions [21]. The combination of the laser heated DAC system and the synchrotron beam provides an ideal tool to study materials at high P-T for understanding the secrets inside the Earth.

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